Marine Chemistry xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Behavior and fluxes of Pt in the macrotidal Gironde Estuary (SW France)

Antonio Cobelo-García [a,*], Daniel E. López-Sánchez [a], Jörg Schäfer [b], Jérôme C.J. Petit [b], Gérard Blanc [b], Andrew Turner [c]

[a] Instituto de Investigacións Mariñas (IIM-CSIC), Vigo, Galicia, Spain
[b] Université de Bordeaux, UMR EPOC 5805, 33615 Pessac, France
[c] School of Geography, Earth and Environmental Sciences, Plymouth University, UK

ARTICLE INFO

Article history:
Received 14 February 2014
Received in revised form 16 July 2014
Accepted 21 July 2014
Available online xxxx

Keywords:
Platinum
Reactivity
Gironde Estuary
Desorption
Fluxes

ABSTRACT

Dissolved and particulate platinum (Pt_D and Pt_P, respectively) have been measured along the salinity gradient in surface water of the Gironde Estuary during two contrasting hydrological regimes; namely, moderate discharge (November 2012) and high discharge (March 2013). During both sets of conditions, Pt_D concentrations displayed maxima but at different locations along the salinity gradient. These observations are attributed to the addition of Pt from suspended particles traversing the estuary, an effect that is kinetically constrained and sensitive to discharge conditions. A minimum in Pt_D concentration in the low salinity range observed under high discharge conditions also suggests that Pt removal may occur in the maximum turbidity zone (MTZ). Particulate Pt also exhibited mid-estuarine maxima, an effect attributed to the presence of anthropogenic Pt in this region, but no clear trend for Pt_P–Pt_D distribution coefficients was evident during either sampling.
Estimated daily gross dissolved (Pt_D) and particulate Pt (Pt_P) fluxes at La Réole, the main fluvial entry to the Gironde Estuary, were 0.018–0.11 mol day^{-1} (3.6–22 g day^{-1}) and 0.001–0.18 mol day^{-1} (0.21–35 g day^{-1}) in November and March, respectively. Using Boyle's method, the daily net Pt_D fluxes from the Gironde Estuary to the coastal ocean were estimated at 0.03 mol day^{-1} (6.5 g day^{-1}) for moderate discharge and 0.17 mol day^{-1} (34 g day^{-1}) during high discharge, reflecting the regime-dependent magnitude of Pt remobilization along the salinity gradient. The findings of the study suggest that estuarine reactivity is of major importance for both the distributions of Pt in estuaries and its export to the global ocean.

1. Introduction

Platinum (Pt), one of the most abundant of the Platinum Group Elements (PGE), is amongst the rarest elements in the Earth's crust, with an average concentration of about 2.6 pmol g^{-1} (or 0.5 ng g^{-1}; Rudnick and Gao, 2003). High chemical resistance and excellent catalytic properties for chemical reactions make Pt an increasingly important component for many technical applications in the chemical, electrical and petroleum industries (Johnson Matthey, 2013). Platinum is also used in catalysts for gasoline and diesel vehicles and is currently being investigated as a potential catalyst in fuel cells of electric cars (APS and MRS, 2011). Additionally, Pt is a component of many cytotoxic anticancer drugs due to the capacity of certain Pt complexes to inhibit cell reproduction by interaction with DNA molecules (Remon et al., 2013). The growing use of Pt and the release of a diversity of chemical forms of the metal, including anthropogenic metallic and oxidic nanoparticles emitted from vehicles along roads and anticancer metabolites emitted from hospitals and in the home, make Pt an emerging transition metal contaminant of particular concern (Schäfer et al., 1999; Curtis et al., 2010; Cobelo-García et al., 2011). Forecasts of increasing release into terrestrial and aquatic systems, coupled with long-distance transport to remote and sensitive areas (e.g. Greenland and Antarctic Ice; Barbante et al., 2001; Soyol-Erdene et al., 2011) warrant closer monitoring and a better understanding of the anthropogenic Pt cycle. With respect to the latter, current estimates suggest that around 85% of the total flux of Pt at the Earth's surface is derived from human activities (Sen and Peucker-Ehrenbrink, 2012).

Because urbanized and industrialized areas are hot-spots of Pt use and emission they represent major sources of the metal to the surrounding aquatic environment via run-off and wastewater release (Ravindra et al., 2004). Once emitted to aquatic systems, however, little is understood about the transport, behavior and fate of Pt or its compounds. In particular, there is a lack of information on the behavior of Pt in estuaries (e.g. Turner, 2007; Turner and Mascorda, 2014) where the nature, fluxes and concentrations of contaminants are often

* Corresponding author at: Instituto de Investigacións Mariñas (IIM-CSIC), Eduardo Cabello 6, 36208 Vigo, Galicia, Spain.
E-mail address: acobelo@iim.csic.es (A. Cobelo-García).

http://dx.doi.org/10.1016/j.marchem.2014.07.006
0304-4203/

modified by a variety of chemical and biological reactions. To this end, the present work provides the first measurements of dissolved and particulate Pt for a major European estuary (Gironde, SW France). The data form the basis of both an examination of the partitioning and geochemical behavior of the metal along the salinity gradient and estimates of its flux from land to ocean under different hydrological conditions.

2. Material and methods

2.1. Study area

The Gironde Estuary, France (~170 km length, ~80 000 km^2 watershed surface area; Fig. 1) is a major European estuary in terms of size and material transport from continent to ocean. Various studies on its physical, hydrological and chemical functioning, including anthropogenically modified trace element cycles, have made it a model fluvial–estuarine system (e.g. Sottolichio and Castaing, 1999; Schäfer et al., 2002). The Gironde Estuary is a meso- to macrotidal estuary and has a mean annual freshwater discharge of ~1000 m^3 s^{-1}. Asymmetrical progression of the tidal wave towards the upstream estuary induces a pronounced maximum turbidity zone (MTZ), with concentrations of suspended particulate matter (SPM) exceeding 1 g L^{-1} in surface water and several hundreds of g L^{-1} in bottom water. The MTZ typically resides in the low salinity region and migrates up and down estuary with seasonal river flow variations (Sottolichio and Castaing, 1999). These hydrological and sedimentary features result in typical water

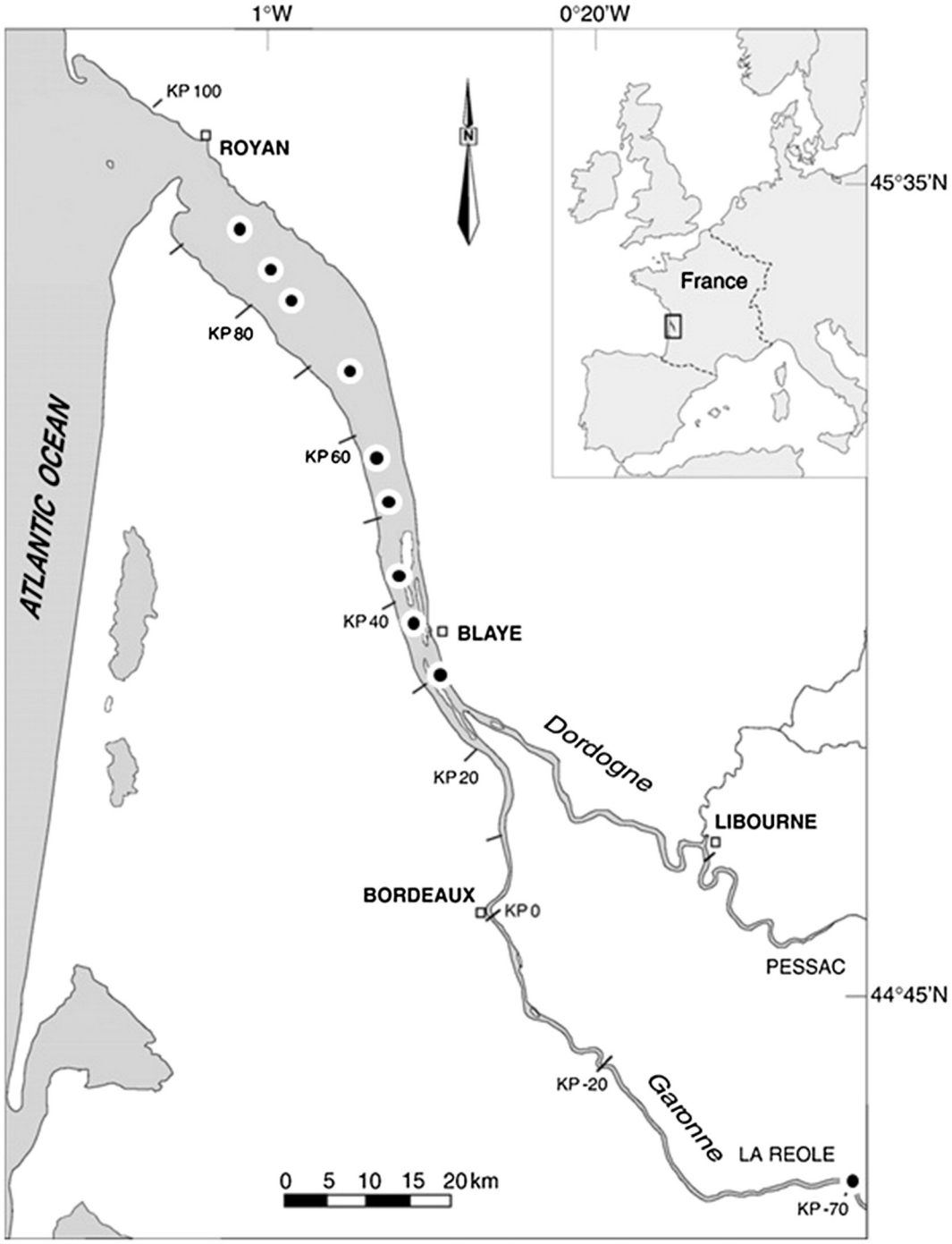

Fig. 1. Map of the Gironde Estuary and fluvial reaches of the Garonne and Dordogne Rivers, with sampling points along the salinity gradient (KP > 20) and at La Réole (KP = −70).

Please cite this article as: Cobelo-García, A., et al., Behavior and fluxes of Pt in the macrotidal Gironde Estuary (SW France), Mar. Chem. (2014), http://dx.doi.org/10.1016/j.marchem.2014.07.006